

# KINETICS OF VACUUM DRYING AND REHYDRATION IN NITROGEN OF COALS FROM THE ARGONNE PREMIUM COAL SAMPLE PROGRAM\*

Karl S. Vorres and Roger Kolman  
Chemistry Division, Building 211  
Argonne National Laboratory  
Argonne, IL 60439

## ABSTRACT

The kinetics of vacuum drying and rehydration in nitrogen of Wyodak-Anderson subbituminous, and Illinois #6 and Utah Blind Canyon high volatile bituminous coal samples have been studied at room temperature. Some samples were oxidized at room temperature. Several cycles of drying and rehydration were carried out on the same sample. The drying rates depended on particle size and moisture content of the sample. Several different mechanisms of moisture loss and rehydration were indicated by the kinetic data. The mechanism depended on particle size, coal rank, and degree of oxidation.

\* This work was supported by the Office of Basic Energy Sciences, Division of Chemical Sciences, U. S. Department of Energy, under contract number W-31-109-ENG-38.

## INTRODUCTION

Drying and rehydration of a porous material can give some insight into the surface properties and the internal structure of the material. The rate of moisture removal or replacement will depend upon the coal surface, the macromolecular network of the coal particles and the structure of the pores through which the moisture flows.

An earlier study (1) reported the results of drying and rehydration studies on Illinois #6 Argonne Premium Coal Samples. The work involved different particle sizes and indicated that the mechanisms of drying and rehydration changed, depending on the coal particle size. The samples were fresh and aged, which also affected the results.

In general four mechanisms were observed (1). One involves a diffusion limited process of migration through a uniform barrier, and is observed with a parabolic curve. This is also referred to as Fickian diffusion. A second mechanism, obeying first order kinetics, similar to radioactive decay, would imply that the probability of a given water molecule being removed or adsorbed was a random probability event, and that all surface sites from which the water molecules depart or the water molecules in the sample were apparently equivalent. The third mechanism gives a plot following an adsorption isotherm curve. The mechanism here depends on the degree of surface coverage. A fourth mechanism, sometimes associated with the parabolic curve, is a linear mechanism implying a uniform barrier for diffusion.

The equation for the diffusion through a growing uniform barrier is:

$$w^2 = kt$$

where  $W$  is the mass change,  $k$  is a rate constant and  $t$  is the elapsed time.

The equation for the first order kinetics is:

$$\log W = k t$$

A characteristic half-time or half-life is associated with this reaction such that half the reaction is over in the half life,  $3/4$  is over in two half lives,  $7/8$  is over in three half lives etc.

For the adsorption or desorption reaction, the equation is:

$$W = k(t/t + 1)$$

A characteristic half time or half life is also associated with this reaction. The half time is the time for half of the observed change to take place. Then  $2/3$  of the reaction takes place in two half times,  $3/4$  takes place in three half times,  $4/5$  takes place in four half times etc.

The equation for the linear reaction is:

$$W = kt$$

This study extended the earlier work and involved examination of the drying and rehydration behavior of a lower rank Wyodak-Anderson sample, and a similar rank (but lower moisture content) sample from a different coal basin (Utah Blind Canyon seam).

#### APPARATUS, MATERIAL AND PROCEDURES

The studies were carried out with an Ainsworth recording thermobalance (described earlier (1)). The samples were weighed on a quartz pan and suspended from the balance. A quartz envelope was placed around the sample to control the gaseous environment. A water bath was placed around the sample to provide for temperature control to about  $1^\circ$  C. Initially the gas atmosphere was removed with a vacuum pump for dehydration. After dehydration, the samples were rehydrated by stopping the vacuum pump, backfilling with nitrogen, removing the quartz envelope, inserting an ice cube, re-evacuating to remove air, and backfilling with nitrogen. The ice cube was melted with warm water, and the water bath was replaced. The cycle was repeated by removing the quartz envelope and water, drying the envelope and replacing it and the water bath. From two to four cycles of dehydration and rehydration with the same sample were obtained in this way.

Sample weights varied between 0.100 and 1.112 grams. The weights used were:

IL #6 Block	1.112 grams
IL #6 -20 mesh	0.100 gram
IL #6 -100 mesh	0.239 gram
Wyodak -20 mesh	0.100 gram
UT Blind Canyon -100 mesh	0.346 gram

The data were recorded on chart paper and estimated to the nearest .01 mg. Buoyancy corrections for going between vacuum and atmospheric pressure were made. Due to some difficulties in establishing the initial weight during the conversions from vacuum to moist nitrogen and vice-versa (due to the rapidity of the change and the sensitivity of the sample to the change in conditions) the nature of the initial mass change is considered somewhat uncertain for some of the pulverized samples.

Data were transferred to a Lotus 1-2-3 file and analyzed on an IBM PC-XT microcomputer. Initial plots were generated from the program.

Some of the analytical data on the samples are as follows:

Sample	Moisture	Ash	Carbon (maf)
Wyodak-Anderson	28.09	6.31	75.01
Illinois #6	7.97	14.25	77.67
Utah Blind Canyon	4.63	4.49	80.69

## RESULTS

The data for the samples was placed on a common basis of mass change in milligrams per gram of sample. The results for the Illinois #6 sample are given in Figures 1-6 for cycles of dehydration or of rehydration for the block, -20 mesh and -100 mesh material, respectively, at room temperature. Figures 7-8 indicate the data for the Wyodak sample at room temperature, while the Figures 9-10 indicate the data for the Utah Blind Canyon for room temperature. The points represent observed data, and continuous lines represent calculated results using the equations for the mechanisms which gave the best fit to the data. Numbers on the figures refer to the cycle of dehydration or rehydration to which the points correspond.

The mechanisms observed are summarized in Table 1.

## DISCUSSION

The dehydration of the Illinois # 6 block followed a set of desorption curves. The amount of water desorbed depended on the amount initially present or returned during the rehydration step. The rehydration #2 was allowed to continue for 3 weeks and indicated that the amount of water which can be adsorbed under those conditions significantly exceeds the ASTM moisture value. The adsorption process is slow and probably would require a number of weeks for a one gram block to reach equilibrium. The desorption mechanism indicates that the rate controlling step involves a loss of moisture from the surface, rather than diffusion from the bulk of the particle to the surface.

The rehydration of the Illinois # 6 block followed a set of parabolic curves, of the type indicating a growing uniform barrier to further diffusion of moisture. This could indicate that the moisture swells the macromolecular network in a manner that uniformly impedes further increase of moisture. The effect of pores for this process is not noticeable.

The dehydration of the -20 mesh material is unique for the samples which have been studied. The initial loss was very low due to the small amount of moisture in the sample at the start. Subsequent runs followed a combination of linear and parabolic segments. The mass change for the initial linear segments increased from cycle 2 to cycle 3. The surface of this sample was oxidized which would provide a number of hydrophilic sites, in contrast to the hydrophobic sites to be expected on pristine samples. The moisture loss is significantly greater than the ASTM moisture value, and a large part takes place in the initial linear segment. This suggests that some moisture may be caught in the interstices of the particles. The ASTM moisture should be the sum of the moisture held in pores and in the macromolecular network. The pore moisture can be approximated by subtracting the amount taken up during the parabolic portion and the final linear part from the ASTM moisture. The amount in excess of the ASTM moisture may approximate the amount held in the interstices between the particles. The interstitial water is expected to be released quickly and following the linear mechanism.

The rehydration of the -20 mesh material was observed to largely follow the adsorption mechanism.

The dehydration of the -100 mesh sample followed the desorption model. The sample had initially been equilibrated with distilled water at room temperature and lost about 11 % moisture. The subsequent rehydration allowed only about 8 % moisture (the ASTM moisture) and that was lost in the following dehydration.

The rehydration curves initially followed an adsorption model and then showed evidence of multilayer formation. However, the subsequent dehydration did not show evidence of separate layers being desorbed.

A comparison of the rates of the reactions showed that the block is the slowest to change mass per gram. The initial rate for the -20 mesh reflects the low initial moisture content of that sample. The intermediate rate was indicated for the -100 mesh material, and the fastest rate for the oxidized -20 mesh material after the initial dehydration. This comparison is valid for both the dehydration and the rehydration mechanisms.

The dehydration data for the Wyodak sample indicated a desorption model.

The rehydration of the Wyodak sample indicated the formation of several layers of moisture following an initial layer of moisture adsorption. Nevertheless, the subsequent dehydration did not show any significant or comparable deviation from the normal desorption curve. The mass loss on the second dehydration indicated that only about 15 % moisture was lost, compared to the 28 % moisture determined by the ASTM method.

The dehydration of the Utah Blind Canyon sample followed the desorption model. The rehydration of the sample also followed the adsorption curve. There was no evidence of multilayer formation.

## CONCLUSIONS

The mechanisms of dehydration and rehydration vary depending on the sample size and history. The behavior of an individual particle is best approximated by the block of Illinois #6 which indicated the desorption mechanism for dehydration and the parabolic mechanism or Fickian diffusion for rehydration. In general pristine samples followed an adsorption or desorption mechanism. Aged or oxidized samples showed combinations of linear and parabolic mechanisms which probably reflect a change in the surface properties in going from a hydrophobic behavior for the more pristine to hydrophilic for the more aged or oxidized material. Multilayer adsorption was observed on the lower rank materials which implies that the functional groups present on the surface facilitate this type of phenomenon.

## ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the Office of Basic Energy Sciences, Chemical Sciences Division, and the Argonne National Laboratory Division of Educational Programs. Tim Griswold helped obtain the data and do some of the data reduction. The glassblowing by Joe Gregar was extremely helpful. Useful discussions with Anthony Fraioli are also acknowledged.

## REFERENCE

1. Vorres, K. S., Kolman, R. and Griswold, T., Preprints, Fuel Chem. Div., Am. Chem. Soc., 33(2), 333(1988)

TABLE 1.

### MECHANISMS FOR THE DEHYDRATION AND REHYDRATION OF COAL SAMPLES.

Sample		Dehydration	Rehydration
Illinois #6	Block	Desorption	Parabolic
	-20 mesh	L - P - L	Adsorption
	-100 mesh	Desorption	Adsorption
Wyodak-Anderson	-20 mesh	Desorption	Adsorption
Utah Blind Canyon	-100 mesh	Desorption	Adsorption

# Vacuum Dehydration of IL #6 Coal Block

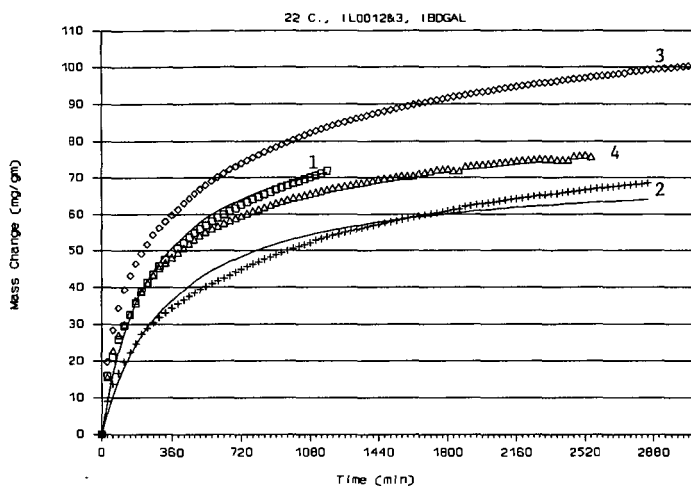


Figure 1.

# Rehydration of IL #6 Coal Block

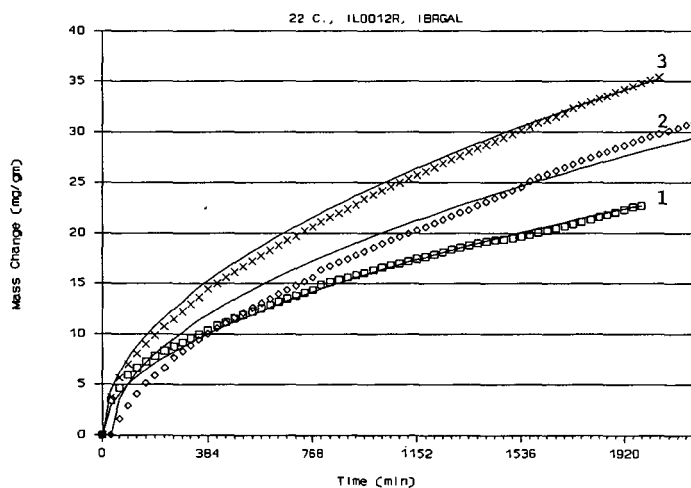


Figure 2.

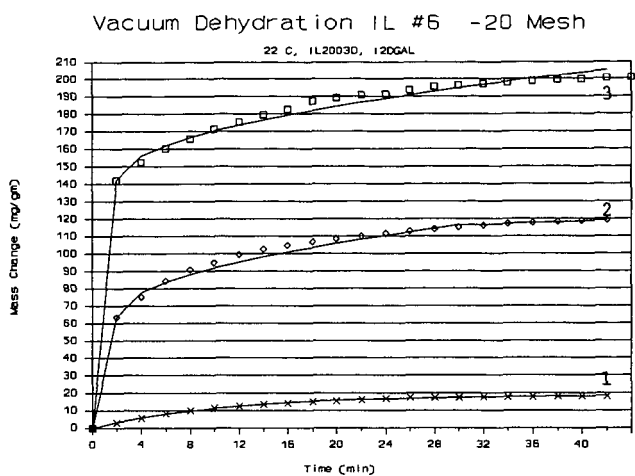


Figure 3.

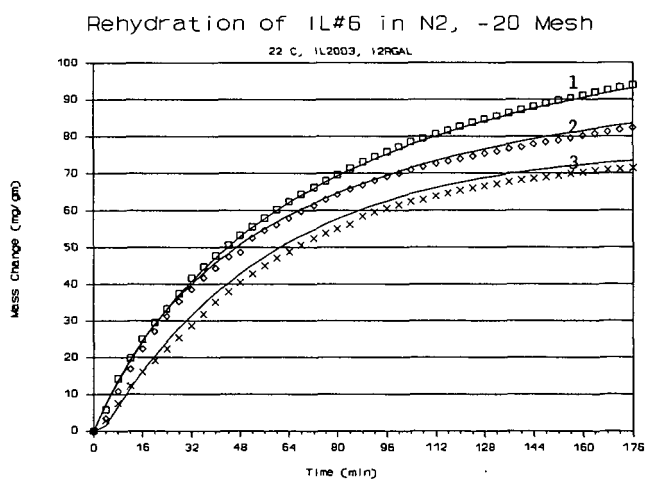


Figure 4.

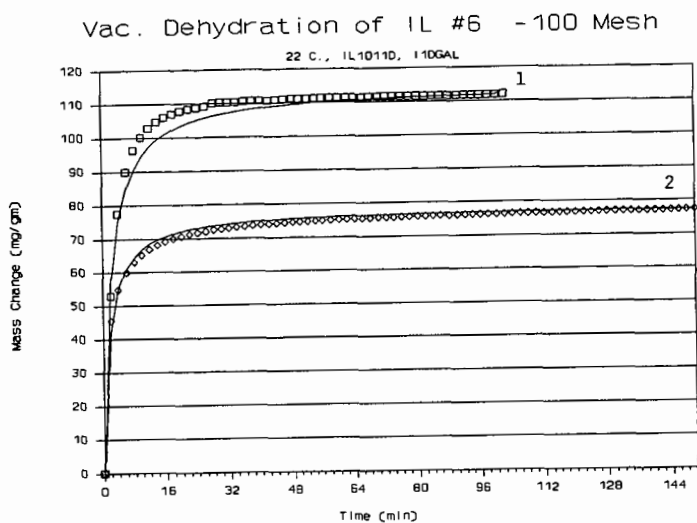


Figure 5.

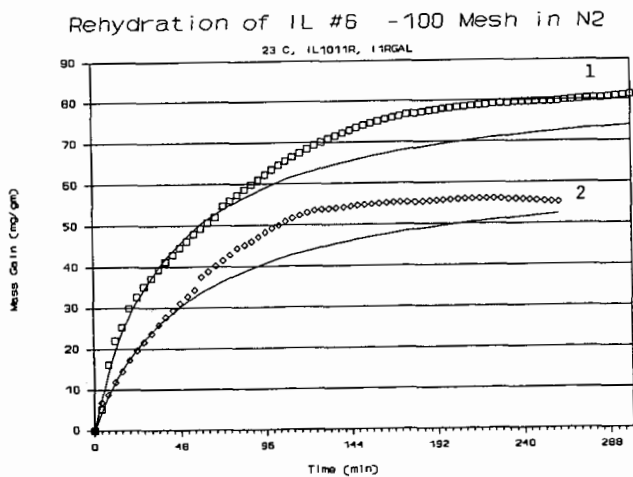


Figure 6.



# Vacuum Dehydration of Wyodak -20 mesh

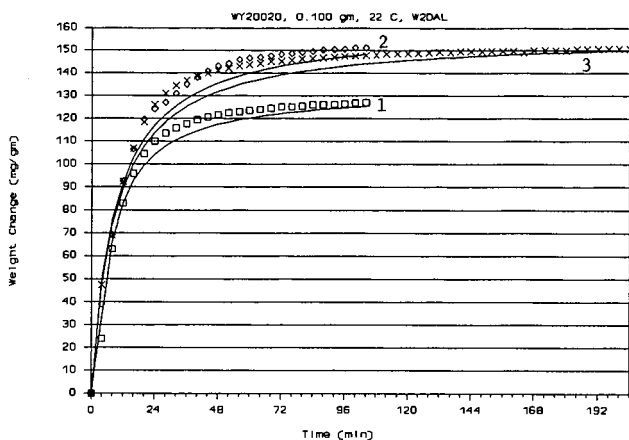


Figure 7.

# Rehydration of Wyodak -20 mesh in N2

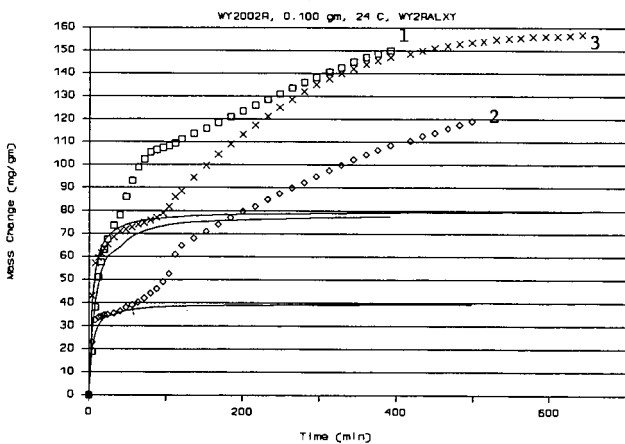


Figure 8.

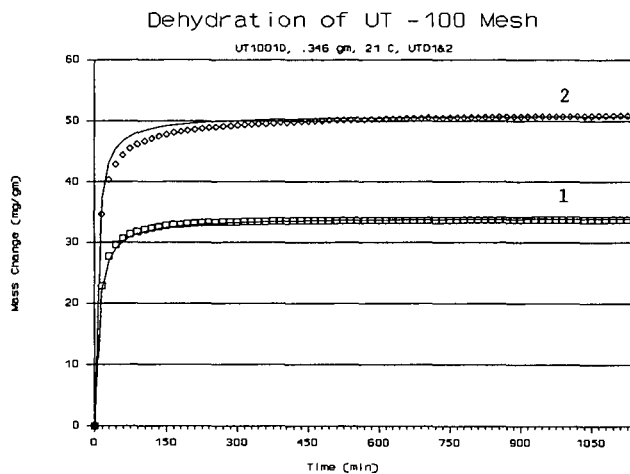


Figure 9.

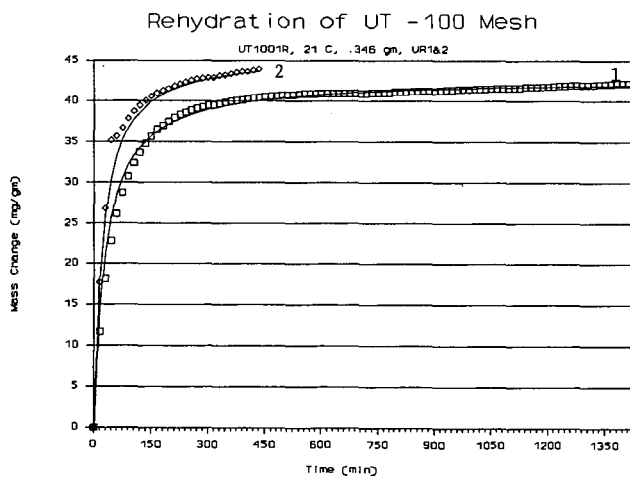


Figure 10.